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Delivery Order 0063: Flexible and Transparent Electronics (FAT) Development

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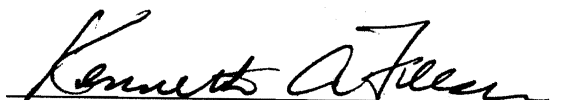
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14. ABSTRACT
This research in support of the Air Force Research Laboratory Materials and Manufacturing Directorate was conducted at Wright-Patterson AFB, Ohio from 20 September 2006 through 31 January 2008. This task exploited the unique electronic and optical properties of nanocrystalline thin metal oxide films to fabricate affordable electronic circuits on large area flexible substrates.

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Executive Summary

This is the final report covering the performance period from 16 September 2006 to 31 January 2008 for the development of flexible and transparent electronics for Air Force sensors applications. During this period major improvements were made to the conductivity and the high temperature stability of transparent conductive films of ZnO by transitioning the growth to Pulsed Laser Deposition (PLD) system and systematically optimizing the growth conditions. We have achieved low resistivity (2.4E-4 ohm-cm) with films that also had high optical transparency (better than 90% from 380nm to at least 2000nm). It was shown that the films were stable in air at high temperatures up to 400°C. Long term stability tests were carried out at 260°C in air for over 2500hr. Breakthrough performance values were achieved with ZnO FETs fabricated on Si, quartz, and GaAs wafers. We have demonstrated current on/off ratios of 10^{12}, current density of 400mA/mm, and sub-threshold current slope value of 109mV/decade. Transistor designs with various gate lengths, gate widths, and gate oxides were investigated to determine scaling rules. It was found that transistor current density stays almost constant with gate width up to 4mm indicating excellent thin film uniformity and device scaling. Finally, we have fabricated and tested world's first microwave thin film ZnO transistors with cut off frequency of 500MHz.

1. Transparent Conductive Film Development

Transparent conductive oxide (TCO) films needed for Air Force sensor applications where Radio Frequency (RF) and Electro-optical (EO) systems need to be co-located for improved system resolution. They are also used in modern display electronics applications including liquid crystal and plasma display panels, solar cells and light emitting diodes (LED).[1] While in most of these applications the incumbent TCO technology is indium-tin-oxide (ITO), there are growing concerns regarding the future availability and cost of ITO films. These concerns are due to the limited availability of the metal indium as the production of consumer products using ITO expand rapidly. Because of these shortage concerns, alternative TCO technologies are being developed. Most of these alternative technologies are also based on amorphous or nanocrystalline oxides of heavy metals with impurity-doped ZnO emerging as the most promising candidate.[2] Using RF sputtering, PLD or Vapor Arc Plasma Evaporation (VAPE), low resistivity Al or Ga-doped ZnO films have been fabricated.[3 4 5 6 7 8] The film resistivities can be further reduced by post-growth annealing in vacuum,[3 9 10] inert gases[11] or hydrogen.[12 13] On the other hand, annealing in oxygen or air at elevated temperatures can increase their resistivity,[14] which promotes the concern of long term reliability of devices operating in air. Modification of the ZnO composition with the addition of other metals as well as the use of layered structures has been shown to improve the resistivity stability at the expense of increased complexity of manufacturing.[15 16] In this project, we have examined the film growth and post-growth annealing parameters to produce films that have low resistivity, high transparency and show excellent stability in air at elevated temperatures.

This effort was a continuation of previous in-house research conducted at the Sensors Directorate of Air Force Research Laboratory. The previous research was concentrated on RF magnetron sputter-deposited ZnO films doped with Al_2O_3 and was able to produce films with the lowest resistivity value of only 6.8E-3 ohm.cm. Since further improvements in resistivity were not possible, we have shifted all efforts to growing films in Pulsed Laser Deposition (PLD) system shown in Figure 1.
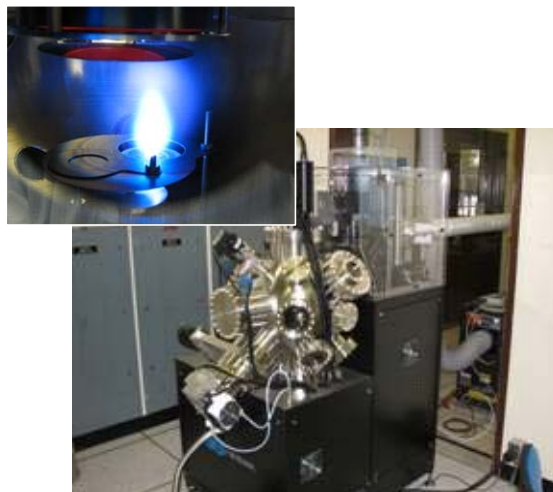
Figure 1. Neocera Pioneer 180 pulsed laser deposition system used for ZnO film fabrication.

Films were deposited in a Neocera Pioneer 180 pulsed laser deposition system with a KrF excimer laser (Lambda Physik COMPex Pro 110, λ=248 nm, 10 ns pulse duration). The chamber base pressure was 4×10^{-8} Torr with oxygen background gas introduced during

deposition to a pressure of 10, 50 and 150 mTorr. The substrate was heated by a backside heater to 350°C as measured with an optical pyrometer and was rotated during deposition. The laser operated at a pulse rate of 4 Hz and an energy density of 2.6 J/cm^2 was measured at the target. The target-to-substrate distance was maintained at 95 mm with a 45° laser angle of incidence to the target. The target was a 50 mm diameter by 6 mm thick sintered oxide ceramic disk (98 wt.% ZnO and 2 wt.% Al_2O_3, 99.999% purity). In conjunction with an off-axis configuration, the laser beam scanned over the rotating target with a synchronized movement of the laser mirror and the focusing/imaging lens.

Films were deposited on thermally-grown SiO_2 covered Si wafers as well as on quartz substrates up to 100mm in diameter. Film thicknesses and refractive indices were measured using a KLA-Tencor P-10 surface profiler and Horiba Jobin Yvon UVISEL spectroscopic ellipsometer. Film thicknesses studied here were in the range of 50 to 500nm with better than 6% uniformity over 3-inch diameter wafers. Film growth conditions were first optimized for uniform and reproducible films by adjusting laser beam conditions, scanning pattern, substrate-to-target distance and substrate temperature. These conditions were not altered for all the samples studied here to maintain film uniformity and reproducibility.

Following film growth, some wafers were annealed in a Steag/Mattson AST100 Rapid Thermal Anneal (RTA) system in N_2 or forming gas, FG (5% H_2 in Ar). Resistivity measurements were made using Transmission Line Method (TLM) with 75µm X 75µm Ti/Au (20nm/350nm) contact pads. This method was found to yield better reproducible resistivity measurements compared to 4-probe method with the added advantage of yielding contact resistance values for this metallization. High temperature stress was applied by placing samples in temperature controlled (±1°C) ovens containing filtered air. Resistivity of each sample was re-measured at room temperature either at the completion of short stress tests or at regular time intervals for long stress tests.

Optical measurements were made on films deposited on quartz substrates using a spectrophotometer (Varian Cary 5000). Both reflection and transmission measurements were acquired using the VW method[17] at a 7-degree angle of incidence. Bandwidths were set such that many substrate fringes were averaged together and therefore high-frequency oscillations were removed. These high-quality films and substrates have negligible scatter therefore we may take the absorption to be 1-*T-R*, where *T* and *R* are the specularly resolved transmission and reflection, respectively. Typical measurements were from approximately 300 nm through 3000 nm. X-ray diffraction data showed that the all films had strong (002) orientation. Crystal size was typically 30nm as determined by Atomic Force and Scanning Electron Microscopes. The crystal size did not show any significant change with growth pressure or with post-growth annealing within the experimental limits discussed here.

As-grown films had resistivity values of 5.2x10^{-3}, 8.2 x10^{-3} and 10.5 x10^{-3} ohm-cm for films grown at 10, 50 and 150mTorr, respectively. Higher resistivity of films grown at higher oxygen pressures is a result of a reduction in both the carrier concentration mobility.[7 10] The reduction in carrier concentration can be due to re-oxidation of Zn interstitials or substitutional Al, which are the main sources electrons. Excess oxygen incorporated at grain boundaries can result in both a carrier concentration reduction in ZnO nanocrystals due to the depletion layer formation and a reduction in carrier mobility due to grain boundary scattering.[7] As shown in Table 1, post-growth annealing in air at 400C for 1hr further increased the resistivity of all 3 films, while annealing in N_2 or FG for 10min decreased resistivity values substantially. In the

absence of grain size change with annealing, the film resistivity variations are most likely due to the change in carrier concentration with the incorporation or the removal of excess oxygen at grain boundaries.[12 18]

Table 1. Resistivity values for 110nm thick AZO films before and after annealing in air, nitrogen and forming gas (FG).

Oxygen Pressure (mTorr)	Film Resistivity (ohm-cm)			
	As Grown	Air, 400°C, 1hr	N_2, 500°C, 10min	FG, 400°C, 10min
10	5.2×10^{-3}	2.9×10^{-2}	6.3×10^{-4}	2.4×10^{-4}
50	8.2×10^{-3}	1.32	7.9×10^{-4}	4.8×10^{-4}
150	10.5×10^{-3}	2.42	9.4×10^{-4}	2.9×10^{-3}

The influence of post-growth anneal in non-oxidizing ambient on film transparency is shown in Figure 2 for films grown at 10mTorr. The average transmittance was 90% from about 380nm to 2500nm wavelengths for as grown films. The N_2 annealed films had improved transmittance in the visible range and no degradation in the infrared region despite of their higher conductivity. The FG-annealed samples also exhibited improvements in transmittance up to 1500nm but showed lower transmittance at longer wavelengths. Nevertheless, the transmittance remained above 80% up to 2500nm in contrast to previous reports where a substantial decrease in transmittance was observed above 1500nm for similar resistivity films.[6 10 19] A slight shift in absorption edge was observed with annealed samples corresponding to a bandgap increase of 60meV and 200meV compared to as-grown films for N_2 and FG annealed films, respectively, as shown in the inset. This increase is consistent with Burstein-Moss-Shift due to increased carrier concentration.[7 20]

The reduction in film resistivity with FG annealing had no significant dependence on the film thickness in the range of 50nm to 400nm. However, as shown in Figure 3, a time-dependent behavior was observed in resistivity for films annealed in FG at 400°C. The film resistivity reached its minimum value within 10 minutes for films grown at 10mTorr pressure. Films grown at higher pressures required longer annealing times to reach their respective minimum values. This is probably due to the differences in the number and/or the adsorptions characteristics of the oxygen atoms influenced by hydrogen. The minimum resistivity values were 6.5×10^{-4}, 3.8×10^{-4}, and 2.1×10^{-4} ohm-cm for films grown at 150mTorr, 50mTorr, and 10mTorr, respectively.
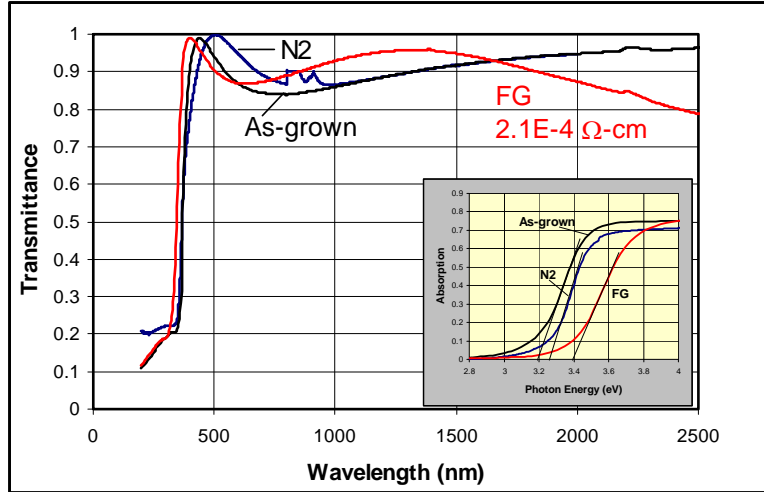
Figure 2. Transmittance and absorption characteristics of 110nm thick AZO films grown at 10mTorr.
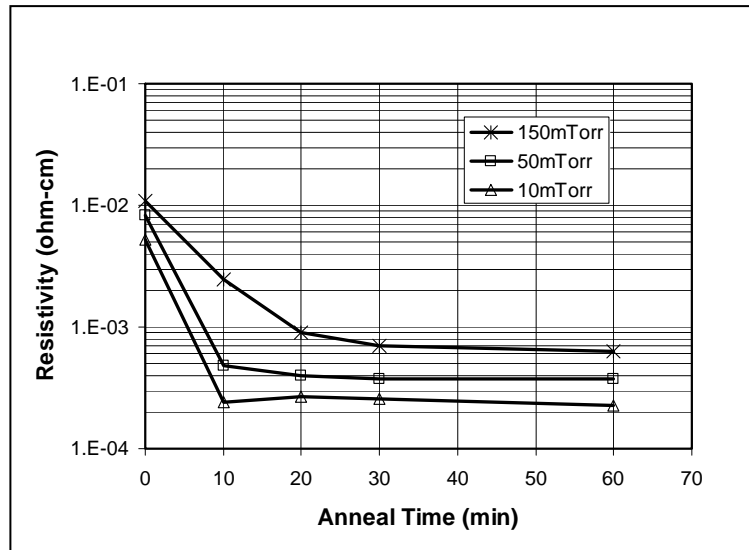

Figure 3. The effect of annealing time on film resistivity for films grown at different oxygen pressures. Annealing was carried out in forming gas at 400°C.

We have conducted stepped-stress tests on films that were annealed in FG at 400°C for 30min to determine their stability in air. Each sample was held at the stress temperature for 2 hours; its resistivity was measured at the room temperature, and then subjected to the next stress temperature. Annealing effects were, therefore, cumulative. The results are shown for films grown at different pressures in Figure 4 (open symbols). The film prepared at 10mTorr pressure maintained its low resistivity up to 300°C, whereas the films grown at higher pressures exhibited sharp increase beyond 200°C. After 400°C tests, the low pressure and higher pressure films had increased their resistivities 2 and 4 orders of magnitude, respectively. The final resistivity values are higher than the as-grown values and are similar to the values obtained by annealing as-grown (i.e. not FG annealed) samples at 400°C in air (see Table 1). These results suggest that not only the hydrogen-related resistivity change has been removed by exposure to oxygen, but additional

oxygen adsorption has taken place. To verify that the increase in resistivity is due to oxygen, we have re-annealed some of the FG-annealed samples in nitrogen instead of oxygen atmosphere and observed no measurable increase in resistivity. In a second verification, we have coated a second set of FG-annealed samples with 80nm of Plasma Enhanced Chemical Vapor Deposited (PECVD) SiO_2 films deposited at 250C and subjected them to the same step-stress tests. The results, also shown in Figure 4 (closed symbols), indicate that this passivation layer retards the impact of oxygen. Passivated samples had more than 2 orders of magnitude lower resistivities after 400˚C stress tests compared to unpassivated samples. The contact resistivity for Ti-Au contacts remained relatively unchanged for all samples at 1×10^{-6} ohm·cm^2 throughout these tests.
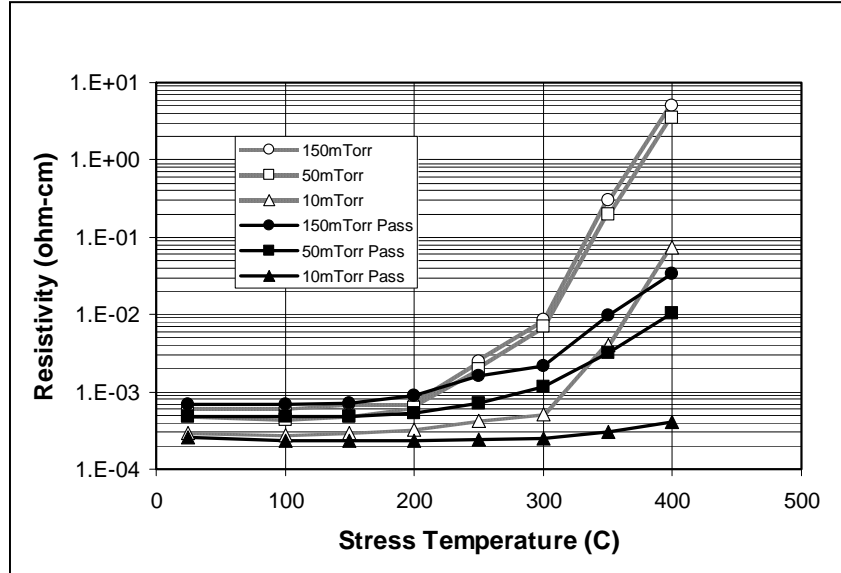

Figure 4. The film resistance change as a function of stress temperature in air. Stress time at each temperature was 2 hrs. Resistivity measurements were made at room temperature.

Although step-stress tests are useful in identifying temperature-activated failure mechanisms, they are insufficient to resolve time-related degradation mechanisms. As a first step in that direction, we have subjected a set of FG annealed and passivated AZO films to long-term stress tests. Figure 5 shows the resistivity value change over 2500 hours for films grown at 10mTorr and 150mTorr. Whereas no change in resistivity was detected for samples prepared at low pressure, about an order of magnitude change was observed with samples prepared at high pressure. The initial rate of change in resistivity is temperature dependent, but eventually the same resistivity values are reached at both temperatures. This behavior can be explained by assuming temperature-dependent oxygen diffusion through the passivation layer and a limited number of sites for oxygen adsorption at the grain boundaries. The results with low pressure grown films indicate minimizing excess oxygen during growth is beneficial to not only lowering the film resistivity but also maintaining it at elevated temperatures in air by possibly minimizing the creation of oxygen adsorption sites at grain boundaries.
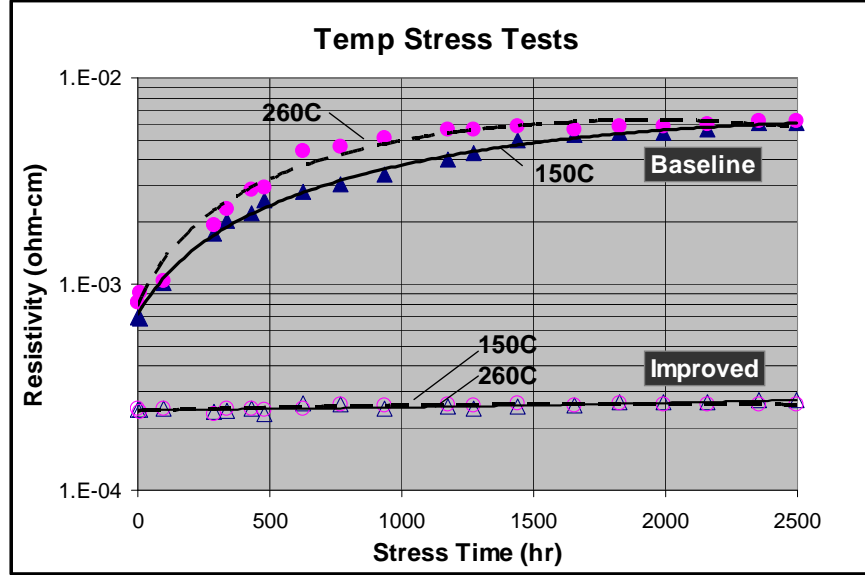
Figure 5. Long-term temperature stress tests for FG-annealed (400˚C, 30min) and passivated films prepared at 10mTorr (improved) and 150mTorr (baseline) oxygen pressures.

In summary, we have investigated the influence of post-growth annealing of PLD-prepared Al-doped ZnO films on film resistivity and the stability of resistivity in air at elevated temperatures. It was found that films grown at lower oxygen pressures can attain lower resistivity values compared to films grown at higher pressures after annealing in forming gas. The high temperature stability of films also shows strong dependence on oxygen pressure and surface passivation. Films prepared at 10mTorr and annealed at 400˚C in forming gas had 2×10^{-4} ohm-cm resistivity and maintained this resistivity for over 2500hr at 260˚C.

2. Thin Film ZnO Transistor Development

Thin film transistors (TFT) are the essential elements of flat panel display electronics. The current technology for this application based on amorphous or polycrystalline Si films has speed limitations due to low mobility of such films. As the demand for higher speed electronics increase with display size and complexity, alternative technologies are being developed based on heavy metal oxide compounds such as ZnO. The increased mobility offered by this technology together with its robustness to environmental conditions, make it a suitable candidate for future applications.[21]

We have developed material deposition and device design approaches to show that ZnO TFT's can offer major improvements in all important device characteristics compared to other similar technologies. Significant improvements were achieved in current on/off ratio ($>10^{12}$), field-effect mobility (>90 cm^2.V^{-1}.s^{-1}), current density (>400mA/mm), sub-threshold slope (100-200mV/decade), and high frequency cut-off frequency values ($f_T=500$MHz and $F_{max}=400$MHz).

ZnO films were deposited in the same PLD system used for transparent conductive films reported above with the exception of target material, which was pure (undoped) ZnO. The system was optimized for uniform films over large area (4-inch wafers). The gate insulator was SiO$_2$ prepared by Plasma Enhanced Chemical Vapor Deposition (PECVD). Devices were fabricated on Si, GaAs and quartz substrates as shown in Figure 6. Although metal gates (Ti)

were used for most devices reported here, some devices were also fabricated on p$^+$-doped Si substrates, which also acted as the gate electrode.

ZnO   Gate   SiO$_2$
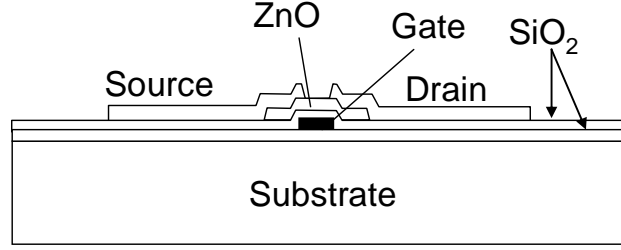
Source   Drain

Substrate

Figure 6. Schematic drawing of ZnO TFT.

Various gate length and width devices were fabricated to establish device scaling uniformity. Typical output characteristics shown for 2 and 3μm gate length devices in Figure 7 indicate that a current density of >400mA/mm of gate width can be achieved. The transfer characteristics, shown in Figure 8, compare the devices with metal and p$^+$-Si gates. Devices with either gate configuration demonstrated >10^{12} current on/off ratios. The only difference between the two devices was a slight shift in threshold voltage. The field-effect mobility calculated from the transfer characteristics, shown in Figure 9, was in the range of 50-95 cm^2.V^{-1}.s^{-1}.

a   **b**
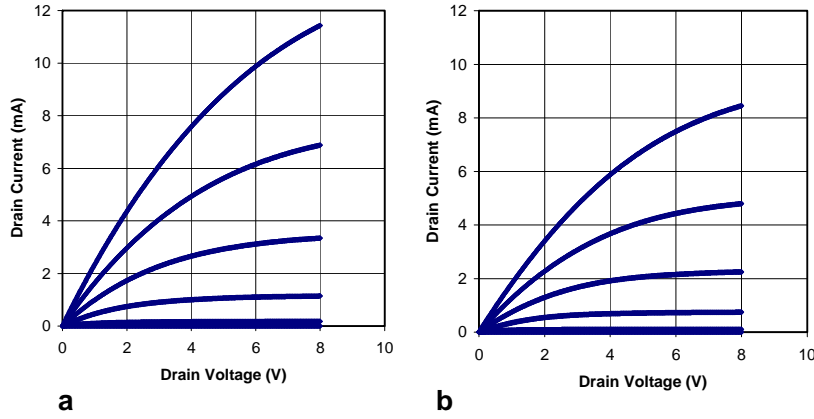
Figure 7. Output characteristics of ZnO TFTs with (a) 2μm and (b) 3μm gate lengths. W=25μm.
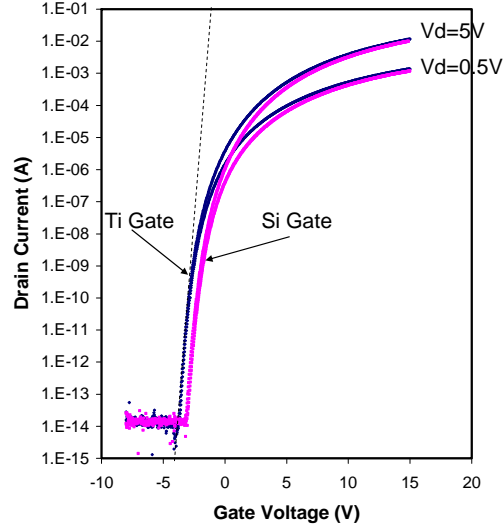
Figure 8. Transfer characteristics of FETs with metal (Ti) and p$^+$-Si gates demonstrating >10^{12} on/off ratio.
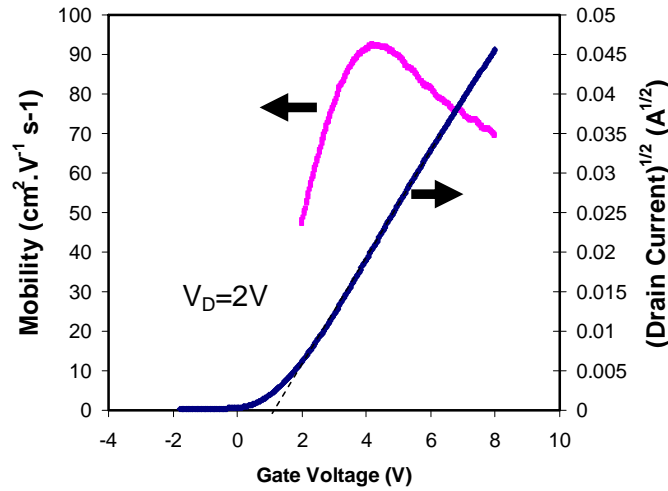

Figure 9. Field effect mobility for FET with W/L ratio of 10 and C_{ox} thickness of 30nm.

The high frequency performance was determined with devices fabricated on semi-insulating GaAs or quartz wafers. Devices with 2 gate fingers (2μm x 25μm) were tested using on-wafer coplanar microwave probes in a HP8751A Network Analyzer. From the measured S-parameters, the current and power gain cut-off frequencies (f_T and f_{max}) were determined, as shown in Figures 10 and 11. Devices fabricated on GaAs substrates had f_T and f_{max} values of 500MHz and 400MHz. These results indicate that ZnO TFT's are attractive alternatives for higher speed display electronics.
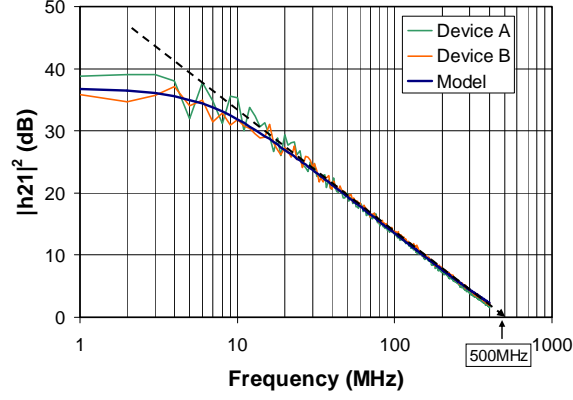
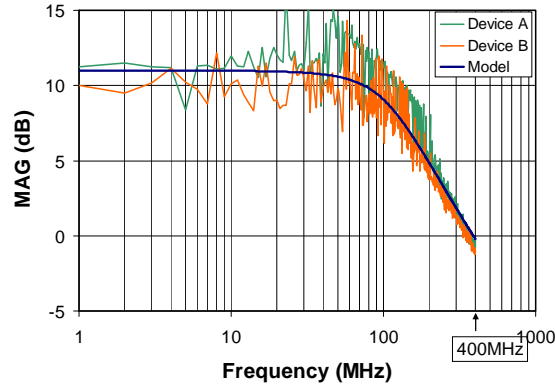*Figure 10. Measured and modeled |h21| as a function of frequency showing f_T=500MHz.*

Figure 11. Measured and modeled maximum available power gain as a function of frequency showing f_{max}=400MHz.

3. Summary and Conclusions

We have achieved low resistivity (2.4E-4 ohm-cm) with films that also had high optical transparency (better than 90% from 380nm to at least 2000nm). It was shown that the films were stable in air at high temperatures up to 400˚C. Long term stability tests were carried out at 260˚C in air for over 2500hr. Breakthrough performance values were achieved with ZnO FETs fabricated on Si, quartz, and GaAs wafers. We have demonstrated current on/off ratios of 10^{12}, current density of 400mA/mm, and sub-threshold current slope value of 109mV/decade, and high frequency cut-off frequency values of f_T=500MHz and F_{max}=400MHz. These are the highest performance values reported for ZnO thin films transistors. Additional improvements can be expected both from transparent conductive films and thin film transistors by refining ZnO growth conditions.

4. REFERENCES

1. H.L. Hartnagel, A.L. Dawar, A.K. Jain, C. Jagadish, Semiconducting Transparent Thin Films, Institute of Physics Publishing, Bristol and Philadelphia, 1995.

2. T. Minami, Semicond. Sci. Technol. **20,** S35–S44 (2005).

3. G. Fang, D. Li and B.L. Yao, Vacuum **68,** p363 (2003).

4. T. Minami, S. Suzuki and T. Miyata, Thin Solid Films **398,** p53 (2001).

5. H. Tanaka, K. Ihara, T. Miyata and H. Sato, J. Vac. Sci. Technol. **A 22(4),** p1757 (2004).

6. H. Agura, A. Suzuki, T. Matsushita, T. Aoki and M. Okuda, Thin Solid Films, **445,** p263 (2003).

7. S.M. Park, T. Ikegami, K. Ebihara and P.K. Shin, App. Surf. Sci, **253**, p1522 (2006).

8. T. Minami, S. Ida and T. Miyata, Thin Solid Films, **416,** p92 (2002).

9. G.J. Fang, D.J. Li and B.L. Yao, Phys. Stat. Sol. A, **193**, p139 (2002).

10. T. Tsuji and M. Hirohashi, Appl. Surf. Sci. **157,** p47 (2000).

11. X. Chen, W. Guan, G. Fang and X.Z. Zhao, App. Surf. Sci. **252,** p1561 (2005).

12. B.Y. Oh, M.C. Jeong, D.S. Kim, W. Lee, and J.M. Myoung, J. Crys. Growth, **281,** p475 (2005).

13. J.F. Chang, W.C. Lin and M.H. Hon, App. Surf. Sci. **183** 18 (2001).

14. T. Minami, T. Miyata, and T.Yamamoto, J. Vac. Sci. Technol. **A 17(4),** p1822 (1999).

15. A. Mitsui and K. Sato, Vacuum **74,** p747 (2004).

16. I.H. Kim, D.Y. Ku, J.H. Ko, D. Kim, K.S. Lee, H.H. Jeong, T.S. Lee, B. Cheong, Y.J Baik, and W.M. Kim, J. Electroceram. **17,** p241 (2006).

17. H. E. Bennett and W. F. Koehler, J. Opt. Soc. Am. **50**, p1-6 (1960).

18. M.L. Addonizio, A. Antonaia, G. Cantele, and C. Privato, Thin Solid Films, **349,** p93 (1999).

19. H. Kim, A. Pique, J.S. Horwitz, H. Mirata, Z.H. Kafafi, C.M. Gilmore. And D.B. Chrisey, Thin Solid Films, **377-378,** p798 (2000).

20. T. Makino, K. Tamura, C. Chia, Y. Segawa, M. Kawasaki, A. Ohtomo, and H. Konuma, Phys. Rev. B, **65,** p121201 (2002).

21. E. Fortunato, P. Barquinha, A. Pimentel, A. Goncalves, A. Marques, R. Martins, and L. Pereira, Appl. Phys. Lett., Vol. **85**, pp.2541-2543 (2004).